

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 February 2003 (27.02.2003)

PCT

(10) International Publication Number
WO 03/016676 A1

(51) International Patent Classification: **E21B 43/16**,
C01B 3/36, 3/38, 13/02, C10G 2/00, C10J 3/00, E21B
43/00

(21) International Application Number: **PCT/EP02/08805**

(22) International Filing Date: **6 August 2002 (06.08.2002)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
01306937.2 **15 August 2001 (15.08.2001)** **EP**

(71) Applicant (for all designated States except US): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V. (NL/NL)**; Carel van Bylandtlaan 30, NL-2596 HR
The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PARSLEY, Alan,
John [GB/AU]**; Level 28 QVI, 250 St. George's Terrace,
Perth, W.A. 6000 (AU). **STOUTHAMER, Christiaan**

[NL/AU]; Level 28 QVI, 250 St. George's Terrace, Perth,
W.A. 6000 (AU).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK,
TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **TERTIARY OIL RECOVERY COMBINED WITH GAS CONVERSION PROCESS**

(57) Abstract: A process for the recovery of oil from a subsurface reservoir in combination with the production of liquid hydrocarbons from a hydrocarbonaceous stream, comprising: (i) separating an oxygen/nitrogen mixture into a stream enriched in oxygen and an oxygen depleted stream; (ii) partial oxidation of the hydrocarbonaceous feed at elevated temperature and pressure using enriched oxygen produced in step (i) to produce synthesis gas; (iii) converting synthesis gas obtained in step (ii) into liquid hydrocarbons; (iv) recovering oil from a subsurface reservoir using at least part of the oxygen depleted gas stream produced in step (i).

WO 03/016676 A1

TERTIARY OIL RECOVERY COMBINED WITH GAS CONVERSION PROCESS

The present invention relates to a process for the enhanced recovery of oil from a subsurface reservoir in combination with the production of liquid hydrocarbons from a hydrocarbonaceous stream.

5 A first element of the present invention concerns the enhanced recovery of oil from a subsurface reservoir.

Enhanced oil recovery (sometimes also called tertiary oil recovery) is the description applied by the oil industry to non-conventional techniques for getting more
10 oil out of subsurface reservoirs than is possible by natural production mechanisms (primary oil recovery) or by the injection of water or gas (secondary oil recovery).

If oil is to move through the reservoir rock to a well, the pressure under which the oil exists in the
15 reservoir must be greater than that at the well bottom. The rate at which the oil moves towards the well depends on a number of features, among which the pressure differential between the reservoir and the well, permeability of the rock, layer thickness and the
20 viscosity of the oil. The initial reservoir pressure is usually high enough to lift the oil from the producing wells to the surface, but as the oil is produced, the pressure decreases and the production rate starts to decline. Production, although declining, can be
25 maintained for a time by naturally occurring processes such as expansion of the gas in a gas cap, gas release by the oil and/or the influx of water. A more extensive description of natural production mechanisms can be found

in the Petroleum Handbook, 6th edition, Elsevier, Amsterdam/New York, 1983, p. 91-97.

5 The oil not producible, or left behind, by the conventional, natural recovery methods may be too viscous or too difficult to displace or may be trapped by capillary forces. Depending on the type of oil, the nature of the reservoir and the location of the wells, the recovery factor (the percentage of oil initially contained in a reservoir that can be produced by natural
10 production mechanisms) can vary from a few percent to about 35 percent. Worldwide, primary recovery is estimated to produce on average some 25 percent of the oil initially in place.

15 In order to increase the oil production by natural production mechanisms, techniques have been developed for maintaining reservoir pressure. By such techniques (also known as secondary recovery) the reservoir's natural energy and displacing mechanism which is responsible for primary production, is supplemented by the injection of
20 water or gas. However, the injected fluid (water or gas) does not displace all the oil. An appreciable amount remains trapped by capillary forces in the pores of the reservoir rock and is bypassed. This entrapped oil is known as residual oil, and it can occupy from 20 to
25 50 percent, or even more, of the pore volume. See for a more general description of secondary recovery techniques the above-mentioned Petroleum Handbook, p. 94-96.

30 Enhanced oil recovery (sometimes called tertiary oil recovery) is the description applied by the oil industry to non-conventional techniques for getting more oil out of subsurface reservoirs than is possible by natural production mechanisms or secondary production mechanisms. Many enhanced oil recovery techniques are known. It covers techniques as thermal processes, miscible
35 processes and chemical processes. Examples are heat

generation, heat transfer, steam drive, steam soak, polymer flooding, surfactant flooding, the use of hydrocarbon solvents, high-pressure hydrocarbon gas, carbon dioxide and nitrogen. See for a more general description of secondary recovery techniques the above-mentioned Petroleum Handbook, p. 97-110.

The use of nitrogen in enhanced oil recovery processes is well known. At first waste gases as stack gas, flue gas and exhaust gas were used. These gasses usually contained not only nitrogen, but also carbon dioxide and optionally steam. See for instance US patent No. 4,499,946. A problem, however, was the presence of certain waste products such as nitrogen oxides and sulphur oxides which give rise to corrosion and pollution problems. A paper by M. D. Rushing et al., entitled "Miscible Displacement with Nitrogen", Petroleum Engineer, November 1977, p. 26-30, describes a miscible oil displacement process involving the injection of high pressure nitrogen. As disclosed, pure nitrogen is injected into the reservoir and functions to initially strip relatively low molecular weight hydrocarbons from the reservoir oil. US patent No. 4,434,852 describes the use of nitrogen and 2 to 20 percent by volume of light hydrocarbons in the enhanced oil recovery of subterranean oil reservoirs. Mixtures of nitrogen and carbon dioxide are described in US patents Nos. 3,811,501 and 4,008,764. The injected gas may take the form of substantially pure nitrogen, such as produced by cryogenic fractionation of air as described by Rothrock et al., Nitrogen Floods Need Specialise Surface Equipment, Petroleum Engineer, August 1977, p. 22-26. As described above, the nitrogen gas may also take the form of flue gasses such as from boilers or internal combustion engines which typically will contain about 80-90% nitrogen, usually 88%, 5-15% carbon dioxide,

usually 10%, 0-2% carbon monoxide, usually 1%, and the remainder hydrogen and trace amounts of other gasses.

As described, attention has been given to producing nitrogen cryogenically. A problem, however, is the need of a large, expensive cryogenic unit.

Several cryogenic concepts have been developed over the years to liquefy and separate air into its main constituents nitrogen, oxygen and rare gases. Refrigeration for cryogenic applications is produced by absorbing or extracting heat at low temperature and rejecting it to the atmosphere at higher temperatures. Three general methods for producing cryogenic refrigeration in large-scale commercial application are the liquid vaporisation cycle, the Joule-Thomson expansion cycle and the engine expansion cycle. The first two are similar in that they both utilise irreversible isenthalpic expansion of a fluid, usually through a valve. Expansion in an engine approaches reversible isenthalpic expansion with the performance of work. For more detailed discussion reference is made to Perry's Chemical Engineers Handbook, Sixth Edition, 12-49 ff. (McGraw-Hill, New York, 1984), Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Edition, Volume 7, p. 662 ff. (John Wiley and Sons, New York, 1993) and Ullmann's Encyclopedia of Industrial Chemistry, Fifth Edition, Volume A 18, p. 332 ff. (VCH, Weinheim, 1991).

Most commercial air separation plants are based on Linde's double distillation column process. This process is clearly described in the above references. In a typical example, feed air is filtered and compressed to a pressure usually between 5 and 10 bara. The compressed air is cooled and any condensed water is removed in a separator. To avoid freezing of water and carbon dioxide in the cryogenic part of the plant, the feed air is further passed through an adsorbent bed, usually

activated alumina and/or molecular sieves, to remove the last traces of water and carbon dioxide. The purified air is then cooled down further, and fed to a first cryogenic distillation unit, usually at an intermediate stage.

5 Crude liquid material from the bottom section of the first distillation unit, usually comprising between 40 and 50 mol percent oxygen, is fed to the second distillation unit (which second unit is usually on the top of the first distillation unit, the condenser of the
10 first column usually acting as the reboiler for the second unit), usually also at an intermediate stage. The second distillation unit is operated at relatively low pressure (usually 1 to 2 bara). At the top of the first distillation unit almost pure liquid nitrogen is obtained
15 which is typically fed to the second column at the top. Pure liquid oxygen is obtained at the bottom of the second distillation unit, while pure gaseous nitrogen is obtained from the top of the second column.

Many variations on the above concept are known. These
20 include separation of air into gaseous products, liquid products and all kind of combinations thereof. Also the production of partly enriched oxygen and/or nitrogen streams together with almost pure oxygen and/or nitrogen streams, either in liquid or gaseous phase is well known.
25 In addition there may be additional distillation units to separate any of the rare gases present in the feed air. Further, the methods for creating the low temperatures may vary in many ways. In this respect reference is made to the above cited literature references, and further to
30 EP 798524, JP 08094245, EP 593703, EP 562893, US 5237822, JP 02052980, EP 211957, EP 102190, SU 947595 JP 71020126 and JP 71020125.

A second element of the present invention concerns
35 the production of liquid hydrocarbons from a hydro-carbonaceous feed.

Many publications are known describing processes for the conversion of (gaseous) hydrocarbonaceous feed stocks, as methane, natural gas and/or associated gas, into liquid products, especially methanol and liquid hydrocarbons, particularly paraffinic hydrocarbons. In this respect often reference is made to remote locations (e.g. in the dessert, tropical rain-forest) and/or offshore locations, where no direct use of the gas is possible, usually due to the absence of large populations and/or the absence of any industry. Transportation of the gas, e.g. through a pipeline or in the form of liquefied natural gas, requires extremely high capital expenditure or is simply not practical. This holds even more in the case of relatively small gas production rates and/or fields. Reinjection of gas will add to the costs of oil production, and may, in the case of associated gas, result in undesired effects on the crude oil production. Burning of associated gas has become an undesired option in view of depletion of hydrocarbon sources and air pollution. Gas found together with crude oil is known as associated gas, whereas gas found separate from crude oil is known as natural gas or non-associated gas. Associated gas may be found as "solution gas" dissolved within the crude oil, and/or as "gas cap gas" adjacent to the main layer of crude oil. Associated gas is usually much richer in the larger hydrocarbon molecules (ethane, propane, butane) than non-associated gas.

In WO 91/15446 a process is described to convert natural gas, particularly remote location natural gas (including associated gas), into liquid hydrocarbons suitable for use as fuel. However, no optimally integrated, efficient, low-cost process scheme has been described.

In WO 97/12118 a method and system for the treatment of a well stream from an offshore oil and gas field has

been described. Natural gas is converted into syngas using pure oxygen in an autothermal reformer, a combination of partial oxidation and adiabatic steam reforming. The syngas (comprising a considerable amount of carbon dioxide) is converted into liquid hydrocarbons and wax. No fully and optimally integrated process scheme for a highly efficient, low capital process is described in this document.

In EP 1 004 746 a process has been described for the combined production of liquid hydrocarbons and the recovery of oil from a subsurface reservoir by partial oxidation of natural gas followed by conversion of the synthesis gas thus obtained into hydrocarbons and separating the hydrocarbons into liquid hydrocarbons and gaseous hydrocarbons (mainly C₁-C₄ hydrocarbons), and combusting and/or expanding these gaseous hydrocarbons to provide power for the secondary or enhanced recovery of oil. However, a further optimisation of the efficiency and the integration of the process is desired.

An object of the present invention is to provide further improvements for an efficient, low cost, process- and energy-integrated process scheme for the production of (easily manageable) liquid and solid hydrocarbons from light hydrocarbons. The further improvement concerns the combined production of hydrocarbons and the enhanced recovery of oil from subsurface reservoirs. It has been found that an efficient process could be developed by separating an oxygen/nitrogen mixture, especially air, into an oxygen rich stream and an enriched nitrogen stream, preferably a pure, i.e. at least 98 vol% pure, nitrogen stream. The oxygen rich stream can be used for the partial oxidation of the natural gas, while the nitrogen stream can be used for enhanced oil recovery. It is observed in this respect that hydrocarbons synthesis starting from synthesis gas made from a hydrocarbonaceous

feed and oxygen made by an air separation unit is well known. However, up till now it has not been realised that the nitrogen, made in the same process, could be used in the enhanced oil recovery. In this respect it is observed that several processes are known for the production of synthesis gas which do not use pure oxygen, such as steam methane reforming and (partly) autothermal reforming. Further, also air may be used in the preparation of synthesis gas. Thus, a number of options for the preparation of synthesis gas for use in the Fischer-Tropsch synthesis are available.

The present invention relates to a process for the recovery of oil from a subsurface reservoir in combination with the production of liquid hydrocarbons from a hydrocarbonaceous stream, comprising:

- (i) separating an oxygen/nitrogen mixture into a stream enriched in oxygen and an oxygen depleted stream;
- (ii) partial oxidation of the hydrocarbonaceous feed at elevated temperature and pressure using enriched oxygen produced in step (i) to produce synthesis gas;
- (iii) converting synthesis gas obtained in step (ii) into liquid hydrocarbons;
- (iv) recovering oil from a subsurface reservoir using at least part of the oxygen depleted gas stream produced in step (i).

The process combines one of the many processes for enhanced oil recovery and one of the possible options for the preparation of hydrocarbons from synthesis gas.

A major advantage of the process over the prior art is that the cheap and clean nitrogen which is produced in the air separation step in order to produce oxygen or oxygen enriched air, is now used in the enhanced oil recovery. This results in a more efficient use of the energy required for the two processes. In addition less capital is needed. Please note that oil and gas fields

are often found in each other neighbourhood. For instance in Nigeria and the Middle East many oil and/or gas fields have been found close to each other. Other regions show the similar patterns. Converting the gas into liquid hydrocarbons in the way as described above, results in a nitrogen stream which now can be used for the enhanced oil recovery of the adjacent oil fields. Thus, disadvantages of other processes and/or the transport of nitrogen over long distances are overcome. As no additional energy is required for the production of the nitrogen, less environmentally unfriendly carbon dioxide is produced. It is observed that up till now the nitrogen produced in an air separation unit is usually vented to the atmosphere. This is at least partly due to the fact that especially gas-to-liquids plants (using so called stranded gas) are usually at remote locations, far away from industrial activities which could use the nitrogen. Up till now no suggestion has been made to use the nitrogen for enhanced oil recovery, while there are sufficient locations at which the nitrogen produced in the air separation unit could be used for enhanced oil recovery. This is the more remarkable as several suggestions has been made as to the use other side products from gas-to-liquids plants, as energy and water.

The separation of the oxygen/nitrogen mixture is suitably carried out according to the cryogenic process as described above. These processes are commercially available, and well known to the man skilled in the art. The oxygen/nitrogen mixture used in step (i) is preferably air. Suitably, the stream enriched in oxygen contains at least 50 mol%, more suitably 85 mol% oxygen, based on the total stream, preferably 95 mol%, more preferably 98 mol%. Suitably the oxygen depleted stream contains at least 95 mol% nitrogen based on the total stream, preferably 98 mol%, more preferably 99 mol%. The

oxygen depleted stream contains at most 2 mol% oxygen based on the total stream, preferably at most 1 mol%, more preferably at most 0.2 mol%. If desired, all traces of oxygen may be removed.

5 The hydrocarbonaceous feed to be used in the present process is suitably methane, natural gas, associated gas or a mixture of C₁₋₄ hydrocarbons, preferably associated gas, more preferably associated gas at a remote location. Other possible hydrocarbonaceous feedstocks are coal,
10 brown coal, peat, heavy hydrocarbons, e.g. crude oil residues, e.g. pitch, and asphaltenes, and bio fuel, e.g. wood, organic waste products and vegetable oils.

 The partial oxidation may be carried out in an oxidation or gasification reactor. A well known process
15 for the partial oxidation of a hydrocarbonaceous feed is the Shell Gasification Process in which the hydrocarbonaceous feed is partially combusted in a non-catalytic process at elevated temperature and pressure. In another embodiment the oxidation is carried out in the
20 presence of a catalyst. Such catalysts are well known in the art and usually comprise one or more noble Group VIII metals. Steam and/or carbon dioxide may be added to the hydrocarbonaceous feed stream in order to adjust the H₂/CO ratio. The oxidation is suitably carried out at
25 temperatures between 900 and 1500 °C, preferably 1000 to 1350 °C, and a pressure between 5 and 120 bar, especially between 25 and 70 bar. Typically the gaseous mixture has an H₂/CO ratio between 1:1 and 3:1, preferably about 2:1. Prior to contacting the gaseous mixture with a catalyst
30 for the conversion of this gaseous mixture into liquid hydrocarbons, it is preferred to remove compounds which could adversely effect the catalyst. In this respect reference is made to the removal of sulphur containing compounds and nitrogen containing compounds (e.g. NH₃ and
35 HCN).

The purified gaseous mixture, comprising predominantly hydrogen and carbon monoxide, is contacted with a catalyst in the catalytic conversion stage, by which these compounds are converted into liquid hydrocarbons. These liquid hydrocarbons may comprise paraffinic hydrocarbons, methanol, aromatic hydrocarbons and the like.

The catalysts used for the catalytic conversion of the mixture comprising hydrogen and carbon monoxide into especially paraffinic hydrocarbons are known in the art and are usually referred to as Fischer-Tropsch catalysts. Catalysts for use in this process frequently comprise, as the catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal. As discussed before, preferred hydrocarbonaceous feeds are natural gas or associated gas. As these feedstocks usually results in synthesis gas having H_2/CO ratio's of about 2, cobalt is a very good Fischer-Tropsch catalyst as the user ratio for this type of catalysts is also about 2.

The catalytically active metal is preferably supported on a porous carrier. The porous carrier may be selected from any of the suitable refractory metal oxides or silicates or combinations thereof known in the art. Particular examples of preferred porous carriers include silica, alumina, titania, zirconia, ceria, gallia and mixtures thereof, especially silica, alumina and titania.

The amount of catalytically active metal on the carrier is preferably in the range of from 3 to 300 pbw per 100 pbw of carrier material, more preferably from 10 to 80 pbw, especially from 20 to 60 pbw.

If desired, the catalyst may also comprise one or more metals or metal oxides as promoters. Suitable metal

oxide promoters may be selected from Groups IIA, IIIB, IVB, VB and VIB of the Periodic Table of Elements, or the actinides and lanthanides. In particular, oxides of magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, cerium, titanium, zirconium, hafnium, thorium, uranium, vanadium, chromium and manganese are very suitable promoters. Particularly preferred metal oxide promoters for the catalyst used to prepare the waxes for use in the present invention are manganese and zirconium oxide. Suitable metal promoters may be selected from Groups VIIB or VIII of the Periodic Table. Rhenium and Group VIII noble metals are particularly suitable, with platinum and palladium being especially preferred. The amount of promoter present in the catalyst is suitably in the range of from 0.01 to 100 pbw, preferably 0.1 to 40, more preferably 1 to 20 pbw, per 100 pbw of carrier. The most preferred promoters are selected from vanadium, manganese, rhenium, zirconium and platinum.

The catalytically active metal and the promoter, if present, may be deposited on the carrier material by any suitable treatment, such as impregnation, kneading and extrusion. After deposition of the metal and, if appropriate, the promoter on the carrier material, the loaded carrier is typically subjected to calcination. The effect of the calcination treatment is to remove crystal water, to decompose volatile decomposition products and to convert organic and inorganic compounds to their respective oxides. After calcination, the resulting catalyst may be activated by contacting the catalyst with hydrogen or a hydrogen-containing gas, typically at temperatures of about 200 to 350 °C. Other processes for the preparation of Fischer-Tropsch catalysts comprise kneading/mulling, often followed by extrusion, drying/calcination and activation.

The catalytic conversion process may be performed under conventional synthesis conditions known in the art. Typically, the catalytic conversion may be effected at a temperature in the range of from 150 to 300 °C,

preferably from 180 to 260 °C. Typical total pressures for the catalytic conversion process are in the range of from 1 to 200 bar absolute, more preferably from 10 to 70 bar absolute. In the catalytic conversion process especially more than 75 wt% of C₅+, preferably more than

85 wt% C₅+ hydrocarbons are formed. Depending on the catalyst and the conversion conditions, the amount of heavy wax (C₂₀+) may be up to 60 wt%, sometimes up to 70 wt%, and sometimes even up till 85 wt%. Preferably a cobalt catalyst is used, a low H₂/CO ratio is used (especially 1.7, or even lower) and a low temperature is used (190-230 °C). To avoid any coke formation, it is preferred to use an H₂/CO ratio of at least 0.3. It is especially preferred to carry out the Fischer-Tropsch reaction under such conditions that the SF-alpha value, for the obtained products having at least 20 carbon atoms, is at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955. Preferably the Fischer-Tropsch hydrocarbons stream comprises at least 35 wt% C₃₀+, preferably 40 wt%, more preferably 50 wt%.

Preferably, a Fischer-Tropsch catalyst is used, which yields substantial quantities of paraffins, more preferably substantially unbranched paraffins. A most suitable catalyst for this purpose is a cobalt-containing Fischer-Tropsch catalyst. Such catalysts are described in the literature, see e.g. AU 698392 and WO 99/34917.

The Fischer-Tropsch process may be a slurry FT process or a fixed bed FT process, especially a

multitubular fixed bed, preferably a three phase fluidised bed process.

Alternatively the gaseous mixture may be converted, using a bifunctional catalyst, in a first step into acyclic hydrocarbons and/or acyclic oxygen containing hydrocarbons. The product formed is at least partially converted in a second step into aromatic hydrocarbons suitable as high octane gasoline and chemical intermediates.

Suitable bifunctional catalysts are known in the art. These catalysts comprise a first catalyst component having activity for the conversion of synthesis gas into acyclic hydrocarbons and/or acyclic oxygen-containing hydrocarbons, such as methanol and dimethyl ether, in combination with a second catalyst component having activity for the conversion of the acyclic compounds mentioned into aromatic hydrocarbons. This first catalyst component comprises at least one metal from the iron group or ruthenium together with one or more promoters to increase the activity and/or selectivity, and sometimes a carrier material such as kieselguhr, such as catalysts containing from 30 to 75 parts by weight iron, and from 5 to 40 parts by weight magnesium per 100 parts by weight alumina. The preparation of the catalyst is similar to that of Fischer-Tropsch catalysts mentioned above. Other suitable catalysts are $\text{ZnO/Cr}_2\text{O}_3$ compositions, in particular such compositions in which the atomic percentage of zinc, based on the sum of zinc and chromium, is at least 60%, and preferably from 60 to 80%. Details of the catalyst and process may be found in the art, for example US patent No. 4,338,089.

Suitable examples of the second catalyst component for the production of aromatic hydrocarbons are crystalline silicates, for instance crystalline aluminium

silicates (zeolites), crystalline iron silicates and crystalline gallium silicates.

The reaction may be carried out at temperatures of from 200 to 500 °C, preferably from 250 to 450 °C, at a pressure of from 1 to 150 bar, preferably 5 to 100 bar, and a GHSV between 50 and 5000 Nl/l/h, preferably 300 to 3000 Nl/l/h.

Alternatively, the gaseous mixture comprising hydrogen and carbon monoxide may serve as a starting material for the preparation of methanol, using any suitable catalytic methanol synthesis process. In this invention methanol is also considered a liquid hydrocarbon.

The recovery of oil from a subsurface reservoir using the oxygen depleted stream as obtained in the first step of the present process is well known to the man skilled in the art. In this respect reference is made to the discussion above concerning the enhanced oil recovery using nitrogen and the references cited. Suitably, nitrogen, optionally in combination with carbon dioxide and/or steam (individually or in selected mixtures) is injected down-hole at controlled temperature and pressure into the formation. Such injections may be continuously with recovery at a production well spaced therefrom, or cyclic with recovery at the injected well ("huff and puff"). The actual requirements will vary from field to field. Temperatures may vary from 20 °C (for miscible light crudes) to 450 °C, or even to 600 °C, for very heavy crudes. Pressures must be in excess of the formation pressure, usually 2 to 50 bar in excess.

The process of the present invention is suitably combined with further additional oil production techniques. In this respect is a preferred embodiment a process in which the oxygen depleted stream is mixed with carbon dioxide. This carbon dioxide is especially

produced in the process in which the synthesis gas
obtained in step (ii) is converted into liquid
hydrocarbons. Carbon dioxide may be present in one or
more (recycle) streams from which it may be extracted, or
5 may be obtained by burning certain waste streams as
Fischer-Tropsch off gas. In another preferred embodiment
of the invention, light hydrocarbons are mixed with the
nitrogen stream. These light hydrocarbons, suitably C₁ to
C₄ hydrocarbons, especially methane, may (at least
10 partly) have been produced in the hydrocarbon synthesis
reaction.

C L A I M S

1. A process for the recovery of oil from a subsurface reservoir in combination with the production of liquid hydrocarbons from a hydrocarbonaceous stream, comprising:

(i) separating an oxygen/nitrogen mixture into a stream enriched in oxygen and an oxygen depleted stream;

(ii) partial oxidation of the hydrocarbonaceous feed at elevated temperature and pressure using enriched oxygen produced in step (i) to produce synthesis gas;

(iii) converting synthesis gas obtained in step (ii) into liquid hydrocarbons;

(iv) recovering oil from a subsurface reservoir using at least part of the oxygen depleted gas stream produced in step (i).

2. A process according to claim 1, in which the oxygen/nitrogen mixture used in step (i) is air.

3. A process according to claim 1 or 2, in which the stream enriched in oxygen contains at least 85 mol% oxygen based on the total stream, preferably 95 mol%, more preferably 98 mol%.

4. A process according to any of claim 1-3, in which the oxygen depleted stream contains at least 95 mol% nitrogen based on the total stream, preferably 98 mol%, more preferably 99 mol%.

5. A process according to claim 4, in which the oxygen depleted stream contains at most 2 mol% oxygen based on the total stream, preferably at most 1 mol%, more preferably at most 0.2 mol%.

6. A process according to any of claims 1-5, in which the hydrocarbonaceous feed is methane, natural gas, associated gas or a mixture of C₁₋₄ hydrocarbons, preferably associated gas.

7. A process according to claim 6, in which the associated gas is associated gas at a remote location.
8. A process according to any of the preceding claims, in which further additional oil production techniques are used.
- 5 9. A process according to any of the preceding claims, in which the oxygen depleted stream is mixed with carbon dioxide.
- 10 10. A process according to claim 9, in which the carbon dioxide is produced in the overall process in which the synthesis gas obtained in step (ii) is converted into liquid hydrocarbons.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/08805

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 E21B43/16 C01B3/36 C01B3/38 C01B13/02 C10G2/00
C10J3/00 E21B43/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 E21B C01B C10G C10J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, TULSA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 769 165 A (DINH VU P ET AL) 23 June 1998 (1998-06-23) column 1, line 35-60 column 2, line 16 column 3, line 24-26 column 4, line 50 -column 6, line 21; figure 1 ---	1-10
X	US 5 388 645 A (PURI RAJEN ET AL) 14 February 1995 (1995-02-14) column 5, line 35-43 column 7, line 63 -column 8, line 35 column 9, line 44 -column 10, line 7 column 11, line 57 -column 12, line 2 ---	1-10
X	US 4 706 751 A (GONDOUIN MICHEL) 17 November 1987 (1987-11-17) column 10, line 51-56; figure 7 ---	1-10
	--- -/-	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

6 November 2002

Date of mailing of the international search report

19/11/2002

Name and mailing address of the ISA
European Patent Office, P.B. 5618 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-3040, Tx: 31 651 epo nl
Fax: (+31-70) 340-3016

Authorized officer

van Berlo, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/08805

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 566 755 A (SEIDLE JOHN P ET AL) 22 October 1996 (1996-10-22) column 16, line 44 -column 17, line 36; claims 1-10 -----	1-10
A	US 4 261 420 A (HITZMAN DONALD O) 14 April 1981 (1981-04-14) column 6, line 16-18; claims 1-6; figure 1 -----	1-10
A	US 6 016 868 A (RIMMER DANIEL P ET AL) 25 January 2000 (2000-01-25) column 13, line 33-61; figures 1-4 -----	1-10
A	NL 8 303 318 A (SHELL INT RESEARCH) 16 April 1985 (1985-04-16) the whole document -----	9,10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 02/08805

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5769165	A	23-06-1998	AU 697189 B2 AU 1241397 A CA 2196376 A1 CN 1165908 A ,B DE 19703401 A1 EA 970010 A1 GB 2309720 A ,B PL 318208 A1 ZA 9700784 A	01-10-1998 07-08-1997 01-08-1997 26-11-1997 07-08-1997 30-09-1997 06-08-1997 04-08-1997 30-07-1997
US 5388645	A	14-02-1995	AU 686266 B2 AU 8077494 A CN 1134179 A ,B PL 315184 A1 WO 9512742 A1 US 5566755 A US 6119778 A ZA 9408596 A	05-02-1998 23-05-1995 23-10-1996 14-10-1996 11-05-1995 22-10-1996 19-09-2000 23-06-1995
US 4706751	A	17-11-1987	CA 1294867 A1 FR 2593854 A1	28-01-1992 07-08-1987
US 5566755	A	22-10-1996	US 5388645 A US 5388642 A US 5388640 A US 5388641 A US 5388643 A US 6119778 A AU 686266 B2 AU 8077494 A CN 1134179 A ,B PL 315184 A1 WO 9512742 A1 ZA 9408596 A AU 694458 B2 AU 8080594 A CA 2175248 A1 PL 315062 A1 WO 9512745 A1 ZA 9408599 A AU 7979294 A WO 9512744 A1 ZA 9408600 A AU 685175 B2 AU 7932994 A CA 2175252 A1 CN 1137816 A ,B PL 315690 A1 WO 9512743 A1 ZA 9408601 A AU 7981994 A WO 9512746 A1 ZA 9408598 A	14-02-1995 14-02-1995 14-02-1995 14-02-1995 14-02-1995 19-09-2000 05-02-1998 23-05-1995 23-10-1996 14-10-1996 11-05-1995 23-06-1995 23-07-1998 23-05-1995 11-05-1995 30-09-1996 11-05-1995 23-06-1995 23-05-1995 11-05-1995 23-06-1995 15-01-1998 23-05-1995 11-05-1995 11-12-1996 25-11-1996 11-05-1995 23-06-1995 23-05-1995 11-05-1995 23-06-1995
US 4261420	A	14-04-1981	NONE	
US 6016868	A	25-01-2000	CA 2335771 A1 WO 9967504 A1	29-12-1999 29-12-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/08805

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
NL 8303318	A	16-04-1985 CA	1250863 A1
			07-03-1989